Indian J. Phys. **64A** (4), 275-280 (1990)

Temperature factors in symmetric and asymmetric molecules

R Somashekar
Department of Physics, University of Mysore, Manasagangotri, Mysore-570 006, India

Received 9 February 1990, accepted 22 March 1990

Abstract : Temperature factors (B) for different groups in symmetric and asymmetric molecules have been computed and compared with those of the other members of the homologous series. One of the perpendicular B-factor components increases with increase in chain-length for symmetric molecules whereas these decrease with increase in chain-length for asymmetric molecules, for the core as well as for the end chains.

Keywords : Temperature factors, Debye-Waller factor, symmetric and asymmetric molecules, liquid crystal.

PACS Nos : 61.10.-i, 61.30.-v, 65.90.+i

1. Introduction

Crystal structure analysis of a series of mesogenic materials consisting of symmetric and asymmetric molecules has been carried out by earlier investigators. The mesomorphic property of a mesogenic material is in fact, connected with the lattice vibrations or atomic vibrations and in turn depends on the temperature factor or Debye-Waller factors. Hitherto no attempt has been made to compare these thermal factors with chain-length for an homologous series for which crystal structure analysis has been carried out. Also, for an homologous series, the thermal factors corresponding to end chains, central bridge portion and benzene groups within the molecule have not been computed and compared with other members.

In the present work, the X-ray temperature factors corresponding to end chains, central bridge portion and benzene groups of a molecule have been computed and compared for two homologous series, namely symmetric (series I) and asymmetric (series II) molecules.

2. Computation of thermal parameters

Symmetric molecules :

P-azoxyanisole (PAA), 4,4′-bis(pentyloxy azoxy) benzene (POAB) and 4,4′-bis-(heptyloxy azoxy) benzene (HOAB) are symmetric and extensively studied subs-

tances. Crystal structures for these compounds have been reported by Krigbaum *et al* (1970), Shivaprakash *et al* (1985) and Leadbetter and Mazid (1979), respectively. All these compounds were found to exhibit nematic phase and corresponding phase transitions have been reported earlier (Somashekar *et al* 1978). These compounds form part of the homologous series I.

Asymmetric molecules :

4,4′-(ethoxy phenyl azo) phenyl valerate, 4,4′-(ethoxy phenyl azo) phenyl hexanoate, 4,4′-(ethoxyphenyl azo) phenyl heptanoate and 4,4′-(ethoxy phenyl azo) phenyl undecylenate are asymmetric molecules. Crystal structure analysis of these compounds have been reported by Shashidhara Prasad *et al* (1979a,b, 1983) and Shaikh *et al* (1984). Also, these compounds exhibit nematic phases and corresponding phase transitions have already been reported (Somashekar *et al* 1978). These compounds form homologous series II. Six thermal factors (B_{11}, B_{22}, B_{33}, B_{12}, B_{23}, B_{13}) for each atom reported in these papers for both symmetric series I and asymmetric series II which forms a symmetric real matrix, have been reduced to three components and statistical average of $\langle B_{\perp}^{1} \rangle$, $\langle B_{\parallel} \rangle$ and $\langle B_{\perp}^{2} \rangle$ correspond-

Table 1. Average temperature factor components for asymmetric molecules in $\AA^2$.

Group	Valerate	Hexanoate	Heptanoate	Undecylenate
$\langle B_{\perp}^{1} \rangle$:				
Chain (right)	12.6 ± 0.1	14.2 ± 1.1	8.7 ± 1.5	7.9 ± 1.1
Benzene	10.3 ± 1.5	9.3 ± 0.8	6.3 ± 0.4	5.3 ± 0.6
Core	9.9 ± 0.1	6.5 ± 0.1	6.2 ± 0.1	5.3 ± 0.1
Benzene	10.5 ± 0.9	7.3 ± 1.1	5.9 ± 0.6	6.2 ± 0.1
Chain (left)	14.1 ± 1.1	10.3 ± 1.5	8.4 ± 0.4	8.4 ± 1.4
$\langle B_{\parallel} \rangle$:				
Chain (right)	2.6 ± 0.2	3.5 ± 0.3	2.9 ± 0.2	2.6 ± 0.5
Benzene	2.9 ± 0.6	3.2 ± 0.8	2.4 ± 0.2	3.4 ± 0.3
Core	2.5 ± 0.1	3.5 ± 0.1	2.4 ± 0.1	3.7 ± 0.1
Benzene	2.4 ± 0.1	3.5 ± 0.3	2.3 ± 0.3	3.6 ± 0.2
Chain (left)	3.1 ± 0.1	3.4 ± 0.4	2.8 ± 0.6	4.0 ± 0.7
$\langle B_{\perp}^{2} \rangle$:				
Chain (right)	5.9 ± 0.3	7.6 ± 1.3	5.6 ± 0.9	5.4 ± 0.5
Benzene	5.4 ± 0.3	4.9 ± 0.4	4.5 ± 0.3	4.2 ± 0.2
Core	5.3 ± 0.4	5.1 ± 0.1	4.7 ± 0.1	4.7 ± 0.1
Benzene	5.6 ± 0.2	5.2 ± 0.5	4.7 ± 0.3	4.3 ± 0.5
Chain (left)	6.8 ± 1.1	5.7 ± 1.0	5.6 ± 0.7	5.2 ± 0.9

ing to end chain, central rigid portion and benzene have been computed using the standard diagonalization procedure (Press *et al* 1986). Here $\langle B_{\perp}^{1} \rangle$ and $\langle B_{\perp}^{2} \rangle$

refer to components (or square of amplitude of vibration) perpendicular to the length of the molecule and one of them lying in the plane of the molecule ($\langle B_{\perp}^{2} \rangle$). Averaged thermal factors corresponding to the end chains, central rigid portion and benzene groups for both symmetric series I and asymmetric series II are given in Tables 1 and 2 along with the estimated standard deviation.

Table 2. Average temperature factor components for symmetric molecules in Å^2.

Group	PAA	Pentyl	Heptyl
$\langle B_{\perp}^{1} \rangle$:			
Chain (right)	8.6 ± 0.9	8.5 ± 2.2	7.3 ± 1.5
Benzene	8.5 ± 0.8	6.3 ± 0.7	6.9 ± 0.4
Core	11.4 ± 0.6	8.3 ± 0.2	7.7 ± 0.6
Benzene	8.4 ± 0.8	6.6 ± 0.9	6.4 ± 0.6
Chain (left)	8.1 ± 1.3	7.1 ± 1.3	9.8 ± 1.5
$\langle B_{\parallel} \rangle$:			
Chain (right)	3.1 ± 0.3	4.0 ± 0.5	3.7 ± 0.4
Benzene	2.7 ± 0.4	3.4 ± 0.2	3.4 ± 0.1
Core	2.5 ± 0.1	3.3 ± 0.1	3.5 ± 0.3
Benzene	2.8 ± 0.2	3.3 ± 0.2	3.7 ± 0.2
Chain (left)	3.1 ± 0.1	3.8 ± 0.5	4.2 ± 0.3
$\langle B_{\perp}^{2} \rangle$:			
Chain (right)	5.4 ± 0.1	6.4 ± 1.5	6.4 ± 0.8
Benzene	4.5 ± 0.6	5.1 ± 0.6	5.4 ± 0.4
Core	4.8 ± 0.4	5.0 ± 0.3	6.1 ± 0.4
Benzene	4.9 ± 0.5	4.3 ± 0.5	5.5 ± 0.4
Chain (left)	5.8 ± 0.1	5.3 ± 1.2	7.9 ± 1.0

3. Results and discussion

The mean temperature factor components $\langle B_{\perp}^{1} \rangle$, $\langle B_{\perp}^{2} \rangle$ and $\langle B_{i} \rangle$ corresponding to the core of the molecule for both symmetric series I and asymmetric series II

Table 3. Variation of observed *B*-factors for symmetric and asymmetric molecules.

Group	Symmetric			Asymmetric		
	Decrease*	Alternation*	Increase*	Decrease*	Alternation*	Increase*
Chain (rihgt)	$\langle B_{\perp}^{1} \rangle$	—	$\langle B_{\perp}^{2} \rangle$, $\langle B_{i} \rangle$	$\langle B_{\perp}^{1} \rangle$, $\langle B_{\perp}^{2} \rangle$	$\langle B_{\parallel} \rangle$	—
Benzene	$\langle B_{\perp}^{1} \rangle$	—	$\langle B_{\perp}^{2} \rangle$, $\langle B_{\parallel} \rangle$	$\langle B_{\perp}^{1} \rangle$, $\langle B_{\perp}^{2} \rangle$	$\langle B_{\parallel} \rangle$	—
Benzene	$\langle B_{\perp}^{1} \rangle$	—	$\langle B_{\perp}^{2} \rangle$, $\langle B_{\parallel} \rangle$	$\langle B_{\perp}^{1} \rangle$, $\langle B_{\perp}^{2} \rangle$	$\langle B_{\parallel} \rangle$	—
Chain (left)	$\langle B_{\perp}^{1} \rangle$	—	$\langle B_{\perp}^{2} \rangle$, $\langle B_{\parallel} \rangle$	$\langle B_{\perp}^{1} \rangle$, $\langle B_{\perp}^{2} \rangle$	$\langle B_{\parallel} \rangle$	—

* with increase in chain length.

are plotted against number of atoms in Figures 1 and 2 respectively. The estimated standard deviation is also shown in figures. Taking the standard deviation into account, we have summarized our observation of variation in B factors with increase

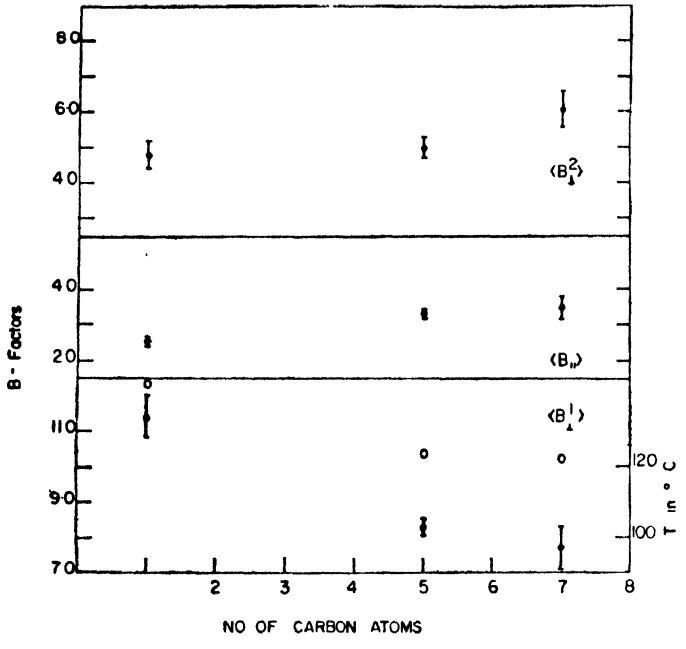

Figure 1. Variation of temperature factors for the core with the number of carbon atoms in symmetric molecules (series I).

O—Transition temperature (nematic-isotropic), $\overset{I}{\underset{1}{\bullet}}$—*B*-factors in Å^2.

in chain length for different regions of the molecule for both symmetric and asymmetric series in Table 3, except for the core which is given in Figures 1 and 2. From the contents of the Tables 1 and 2, the differences (Δ's) between the thermal parameters of adjacent members of the homologous series, the corresponding estimated standard deviations (e.s.d.'s $\sigma(\Delta)$'s) and the ratios $|\Delta|/\sigma(\Delta)$ which represent the statistical significance of the observation are generally above 1σ level except for a very few cases in asymmetric series. This particular observation cannot be carried out on symmetric series because the data on the series is incomplete. For both symmetric and asymmetric molecules, there is a general trend of decrease in the values of $\langle B_{\perp}^{1} \rangle$ component with increase in chain-length. The observed decrease in nematic-isotropic transition temperature for both symmetric and asymmetric molecules is due to the fact that in both cases the values of $\langle B_{\perp}^{1} \rangle$ decrease with increase in chain-length. For asymmetric molecules $\langle B_{\parallel} \rangle$ shows a alternation with increase in chain-length which is in conformity with observed variation of nematic-isotropic transition temperature. Since the data is not

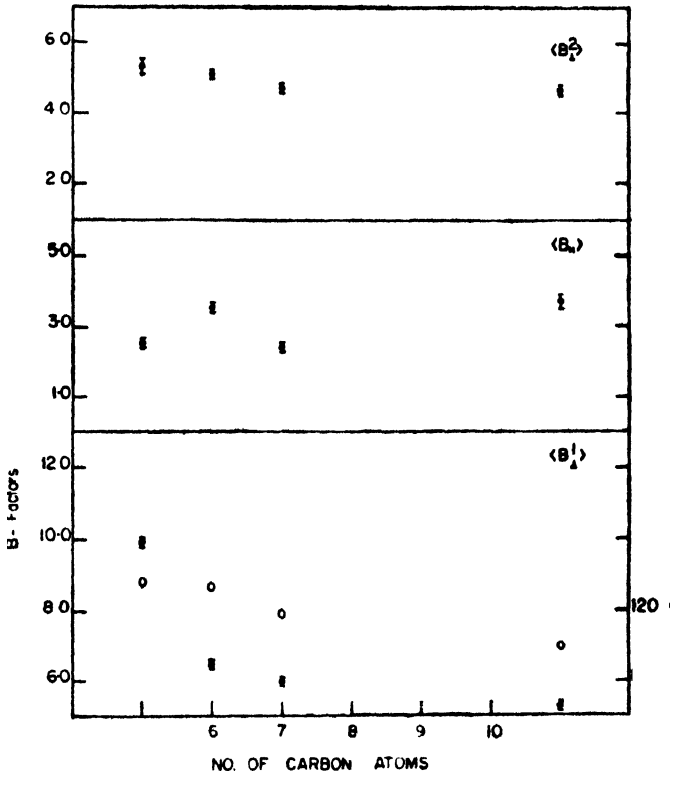

Figure 2. Variation of temperature factors for the core with the number of carbon atoms in asymmetric molecules (series II).

O—Transition temperature (nematic-isotropic), $\overset{1}{\underset{1}{\bullet}}$—*B*-factors in Å^2.

complete for symmetric molecules, it is not possible to arrive at any conclusion for symmetric molecules with regard to alternation in $\langle B_1 \rangle$ components. Also, it emerges from these calculations that the addition of methylene group to one of the end chain in series II (right side of the core) affects not only its vibration but also the vibration of the other end chain (left side of the rigid core). It is evident that the parallel component of temperature factor is very much less compared to transverse components of temperature factor indicating that the transverse vibrations of the molecule play an important role with regard to the transition temperature whenever methyl group (CH_2) is added or subtracted in the end chain. This is in agreement with the notion that the side-side interaction of the molecules are essential in understanding the mesomorphism.

4. Conclusions

The results obtained here clearly emphasis the fact that for both symmetric and asymmetric molecules, the transverse vibrations of the molecule play an important

role in determining the transition temperature from the liquid crystalline phase to the isotropic phase.

Acknowledgments

Author would like to thank the International Crystallography Union, England, for supplying the data and to Professor J Shashidara Prasad for preprints.

References

Krigbaum W R, Yozo Chatani and Barber G P 1970 *Acta Cryst.* **B26** 97

Leadbetter A J and Mazid M A 1979 *Mol. Cryst. Liq. Cryst.* **51** 85

Press W, Flannery B P, Tenkelsky S and Vetterling W T 1986 *Numerical Recipes* (England : Cambridge University Press) p 349

Shaikh A M, Shivaprakash N C, Abdoh M M M and Shashidhara Prasad J 1984 Z. *Kristallogr.* **169** 109

Shashidhara Prasad J 1979a *Acta Cryst.* **B35** 1407

——1979b *Acta Cryst.* **B35** 1404

Shashidhara Prasad J, Abdoh M M M and Shivaprakash N C 1983 *Mol. Cryst. Liq. Cryst.* **103** 261

Shivaprakash N C, Abdoh M M M and Shashidhara Prasad J 1985 Z. *Kristallogr.* **172** 79

Somashekar R, Revannasiddaiah D, Madhava M S, Subramhanyam H S and Krishnamurti D 1978 *Mol. Cryst. Liq. Cryst.* **45** 243